

Title: HIGHLY SELECTIVE H₂ SEPARATION ZEOLITE MEMBRANES FOR COAL GASIFICATION MEMBRANE REACTOR APPLICATIONS

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1. ABSTRACT

Objective

Zeolites are microporous crystalline aluminosilicates, having cage-like structures of precise geometry with pores of uniform shape; zeolites are capable of molecular sieving. The objective of this research is to develop zeolite membranes that are capable of highly selective H₂ separation from other light gases (CO, CO₂ and CH₄) for use in catalytic membrane reactor applications related to coal conversion and gasification. These zeolite membranes have the potential to operate over a wide temperature and pressure range and in chemically challenging environments where existing technologies are inefficient or unable to operate.

Accomplishments to Date

To obtain high selectivity for H₂ separation at elevated temperatures over other light gases, the membranes must be able to discriminate between molecules that are approximately 0.3-0.4 nm in size and 0.1 nm or less in size difference. To date, zeolite membranes have not been made very successful to achieve this sieving because the membranes synthesized either have zeolite pores too big for H₂ separation or contains too many defects. To decrease the zeolite pore size and/or the number of defects within the zeolite membranes, we used silylation reaction to post-treat the as-synthesized zeolite membranes. In this reaction, methyl-diethoxysilane (MDES) was firstly chemisorbed onto the acid sites within the zeolite membrane, then catalytically cracked on sites and oxidized. As a result, additional silicon atoms were added to the original zeolite structures, and the effective pore opening size of the defects and/or zeolite pores was decreased. Two different types of zeolite membranes have been silylated: medium pore MFI membranes with ten-membered ring structure and small pore SAPO-34 membranes with eight-membered ring structure. The silylation reaction could reproducibly improve the hydrogen separation performance for both types of zeolite membranes.

For MFI type zeolite membranes with plenty of acid sites, MDES could penetrate into the medium-sized zeolite pores. Thus, after silylation, the zeolite pores were partially blocked. As a result, hydrogen selectivity over other light gases (CO₂, CO, CH₄, N₂, O₂) all increased. The H₂/CO₂ ideal selectivity can be as high as 235 for the silylated MFI membranes, as compared with only 1.8 for the original membrane. The H₂ permeance however, decreased more than an order of magnitude. For H₂/CO₂, and H₂/CH₄ binary mixtures, The H₂/CO₂ separation selectivity at 473 K increased from 1.4 to 37, whereas the H₂/CH₄ separation selectivity increased from 1.6 to 33. The membranes became

more promising at higher temperatures, as the H₂ permeance as well as separation selectivity increased with increasing temperatures. At 673 K, the H₂ permeance was $1.0 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$, and the H₂/CO₂ separation selectivity was 47. Above 673 K, the silylated MFI membrane catalyzed the reverse water gas shift reaction and still can selectively separate H₂ from CO₂ and CO. For MFI membranes with no acid sites, the silylation reaction did not change their hydrogen separation performance

For SAPO-34 membranes, MDES did not penetrate into the zeolite pores due to the small zeolite pore size. So only the bigger non-zeolite defects were affected. As a result, hydrogen permeance was almost unchanged after silylation. The silylation reaction increased the membrane H₂/CH₄ separation performance, and separation selectivity can be increased more than 50% from 35 to 59. The H₂/CO₂ and H₂/N₂ separation selectivities, however, did not change much. The silylation reaction is also effective in improving CO₂/CH₄ separation performance of the SAPO-34 membrane. The CO₂/CH₄ separation selectivity could be improved from 73 to 110, with the CO₂ permeance deduction of about 20%.

Future Work

- Obtain gas adsorption isotherms and the chemical structures of zeolite powders before and after silylation in order to understand the underlying factors that cause gas transport changes.
- Synthesize thinner zeolite membranes and mask lower part of the membrane pores before and during silylation in order to increase H₂ flux through the silylated membranes
- Try separation of syngas mixtures in the presence of water at elevated pressures

2. LIST OF PAPER PUBLISHED, U.S. PATENT/PATENT APPLICATION(S), CONFERENCE PRESENTATIONS, STUDENTS SUPPORTED UNDER THIS GRANT

List of Paper Published

Modification of Zeolite Membranes for H₂ Separation by Catalytic Cracking of Methyl-diethoxysilane, M. Hong, R.D. Noble, J.L. Falconer, *Ind. Eng. Chem. Res.*, under revision

Conference Presentations

Modification of B-ZSM-5 Zeolite Membranes for Improved Hydrogen Separation, M. Hong, R.D. Noble, J.L. Falconer, 16th Annual Meeting of the North American Membrane Society, June 11-15, 2005, Providence, RI, Submitted

Light gas separations through silylated zeolite membranes, M. Hong, R.D. Noble, J.L. Falconer, 3rd international zeolite membrane meeting, July 25-28, 2004, Breckenridge, CO

Awards Received as a Result of Supported Research

Modification of MFI zeolite membranes by silylation for H₂ separation, M. Hong, StAR Symposium, Department of Chemical and Biological Engineering, University of Colorado, February 5, 2004, third place, Boulder, CO

Students Supported Under This Grant

Mei Hong, graduate student in the Department of Chemical and Biological Engineering, University of Colorado.